

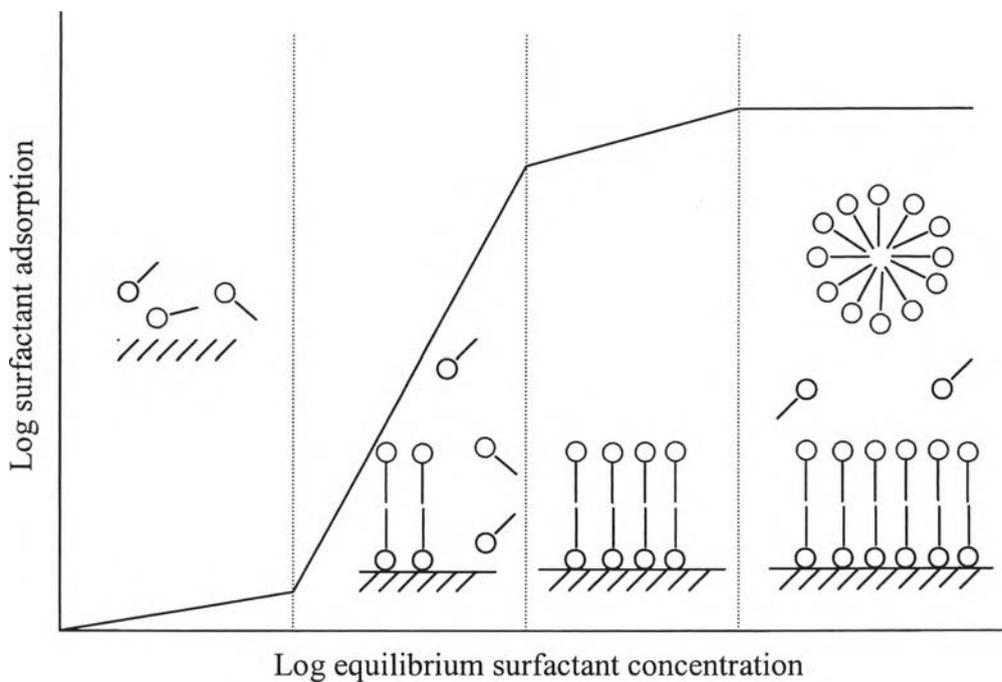


## CHAPTER II

### BACKGROUND AND LITERATURE REVIEW

#### 2.1 Adsorption of Surfactant on Solid Oxide Surface.

The adsorption isotherm of an ionic surfactant onto an oppositely charged substrate, for example, sodium alkanesulfonates and alkybenzenesulfonate oppositely charged  $\text{Al}_2\text{O}_3$ , is typically S-shaped (Scamehorn *et al.*, 1982). The shape of the isotherm is believed to reflect four distinct modes of adsorption as shown in Figure 2.1.



**Figure 2.1** Typical adsorption isotherm of surfactant on solid oxide surface.

Region I corresponds to both very low concentration and low adsorption of surfactant. This region is commonly referred as the Henry's law region because the adsorbed surfactant is considered to be in infinite dilution in the solid phase and, thus, the interaction between molecule of surfactants is negligible. Adsorbed surfactants in this region are viewed as being adsorbed alone and not forming any aggregates. For nonionic surfactant and for ionic surfactant with some added electrolyte, the slope of the isotherm of this region is one when the data is plotted on the log-log plot (Rosen, 1988). For ionic surfactant on a surface of moderate charge density with no added electrolyte, the slope of the isotherm may be less than one because the charge on the surface is being reversed by the adsorption of the charge surfactant ions. In many systems where conditions are favorable to surfactant adsorption, this region may not even be detectable because it occurs at such low surfactant concentrations, i.e., below the detection limits of many methods.

Region II is distinguished by a sharp increase isotherm slope relative to the slope in the region I. The adsorption increases rapidly beyond a certain concentration. At this concentration, hemimicelles resulting from lateral interaction between adsorbed surfactant first appear on the most energetic surface patches (Scamehorn, 1982). These adsorbed surfactant aggregates are called admicelles or hemimicelles, depending upon whether the aggregates are viewed as bilayer or monolayer. The admicelle is a local bilayer structure with a lower layer of head groups adsorbed on the substrate surface and an upper layer of head groups exposed to the solution. The hemimicelle is a monolayer structure having the head group adsorbed on the surface while the tail group exposed to the solution (Yeskie and Harwell, 1987).

The slope of the isotherm decreases in region III. This is thought to be caused by repulsion between the like-charged head groups on the surface or the beginning of adsorption on lower energy surface patches (Tiberg, 2000). While in region II surfactant molecules are adsorbing onto the higher energy sites on the substrate surface. The region II/region III transition does not always correspond to a change in the charge of the surface, however it is also observed in systems of nonionic surfactant adsorbed on silica (Rosen, 1988). Other works have attributed the mechanism for the change in the slope from region II to region III. The most

commonly given explanation is that the aggregates forming in region II are monolayers adsorbing head down on an oppositely charged surface (Rosen, 1988). The change in slope coincides with the cancellation of the charge on the solid surface by the charge on the adsorbed aggregates so that subsequent surfactants are adsorbing onto a like-charged surface. It is also proposed that a second layer on the aggregate does not begin to form until region III occurs (Rosen, 1988).

The region IV is the plateau adsorption region and occurs at concentrations above the critical micelle concentration (CMC). This region is characterized by near zero slope (Scamehorn, 1982). In most systems the region III/region IV transition occurs near the CMC of the surfactant (Rosen 1988). When the surfactant is monoisomeric, the adsorption becomes nearly constant above the CMC. This phenomenon is easily understood in terms of the pseudophase separation model of micelle formation: micelles that form at the CMC have the same chemical potential as the monomer at the CMC. As the concentration of surfactant increases, the surfactant molecules go into the micellar pseudophase at almost the same chemical potential as the surfactant in the first micelle to form and so the chemical potential of the surfactant does not increase as dramatically which surfactant concentration above the CMC as it would in the absence of micelles. Since the admicelles are also in equilibrium with the same monomer phase, the last admicelle to form is also at the same chemical potential as the monomer at the CMC. The only way more admicelles can form is for the chemical potential of the surfactant to increase, but this occurs only slowly because the surfactant added above the CMC form more micelles at the nearly the same chemical potential as that of the micelle that formed near the CMC. The pseudophase separation model is certainly only an approximation, but in general, the better a surfactant is at forming micelle, the more pronounce will be the regionIII/regionIV transition, the closer that transition will be to the CMC, and the less the adsorption will increase above the CMC (Scamehorn *et al.*, 1981).

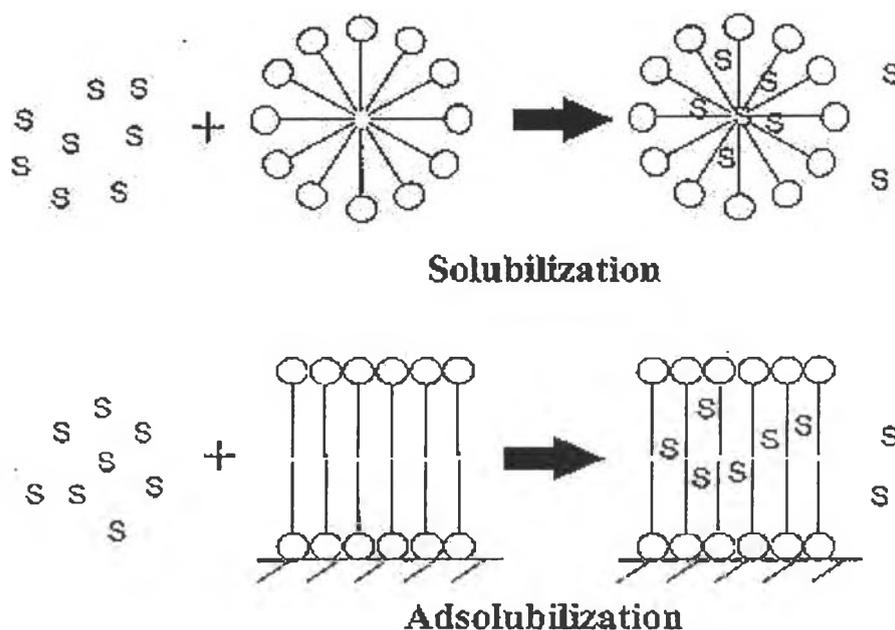
Yeskie and Harwell (1988) studied the structure of the adsorbed surfactant aggregates, focusing on the surface charge density at the hemimicelle/admicelle transition. They found that surfactants adsorbed from aqueous solution onto mineral oxide surfaces formed micelle-like aggregates at the interface. It has long been

viewed that at low coverage these surfactant aggregates are principally in the form of monolayers, formed on patches of the surface. Individual surfactant molecules or monomers in these aggregates are viewed as being oriented such that the hydrophilic groups of the surfactants are next to the surface, with the surfactant tail groups forming a hydrophilic film in contact with the aqueous solution. Aggregates of this structure are commonly referred to as hemimicelles while it has been proposed that a bilayered aggregate, termed an admicelle, is formed (Scamehorn *et al.*, 1981).

## 2.2 Solubilization and Adsolubilization

Solubilization is defined as the spontaneous dissolving of a substance (solid, liquid or gas) by reversible interaction with the micelle of the surfactant in a solvent to form a thermodynamically stable isotropic solution with reduced thermodynamic activity of the solubilized material (Rosen 1988). The suggested definition of adsolubilization is “the incorporation of compounds into surfactant surface aggregates, which compounds would not be in excess at the interface without surfactant.” (Scamehorn and Harwell, 1988). This phenomenon is the surface analog of solubilization, with adsorbed surfactant bilayer playing the role of micelle, as shown in Figure 2.2.

Kitiyanan *et al.* (1996) studied adsolubilization of styrene and isoprene into cetyltrimethylammonium bromide (CTAB) admicelle on precipitated silica. The results from single adsolubilize systems showed that styrene adsolubilization increases with increasing styrene equilibrium concentration in aqueous phase, and isoprene adsolubilization increases with increasing isoprene partial pressure. The adsolubilization equilibrium constants of both adsolubilizates were calculated, and suggested that styrene is adsolubilized into both the palisade layer and the core of admicelle, while isoprene is adsolubilized only into the palisade layer.



**Figure 2.2.** The phenomena of solubilization and adsolubilization.

Lai *et al.* (1997) investigated sodium perfluoroheptanoate adsorption and adsolubilization of small aliphatic fluorocarbon alcohols into surface aggregate formed on alumina. They found that higher concentrations and increasing hydrophobicity of the solutes enhanced surfactant adsolubilization below the plateau region. Partitioned amounts of the fluorocarbon alcohols rose with the alcohol supernatant concentration and chain length. Aggregation numbers were estimated by using the two-site adsolubilization model.

Thakulsukanant *et al.* (1997) studied adsolubilization characteristics and stability characteristics of hydrocarbon aggregates chemically bonded to porous silica. In this study, octadecyltrichlorosilane (ODS) was chemically bonded with silanol groups of silica surface. The adsolubilization capabilities and stability of the bonded ODS were evaluated and compared to those of physically adsorbed aggregates of cetyltrimethylammonium bromide (CTAB). The adsorption of ODS increased with increasing ODS concentration in the bulk phase and reached a constant value when the equilibrium ODS concentration was higher than 1700  $\mu\text{M}$ .

Holuzheu *et al.* (2000) studied the distribution ratios of aromatic compounds between aqueous solution and surfactant-covered silica by chromatographic method. In this work equilibrium constants of 26 aromatic compounds were determined by a chromatographic method as functions of pH and of the adsorption density of hexadecyltrimethylammonium bromide (HDTMAB) on silica. The dependency of the retention time on surfactant adsorption changed with increasing HDTMAB coverage and was modified by pH. The changes could be explained by the transition of electrostatically driven surfactant adsorption to hydrophobic aggregation.

### **2.3 Factors Affecting Surfactant Adsorption and Adsolubilization.**

The adsorption of surfactants at the solid-liquid interface is strongly influenced by a number of factors. Three important factors are being discussed here:

#### **2.3.1 Nature of the Structural Groups on the Solid Surface**

Adsorption of surfactant on solid surface is related directly to the nature and number of the structural groups on the solid surface responsible for the adsorption whether the surface contains highly charged sites or essentially nonpolar group, and the nature of the atoms of which these sites or grouping are constituted.

In 1999, Chorro *et al.* studied the effect of the state of the silica surface and of the surfactant molecular structure on the adsorption of cationic surface onto silica. The adsorption of DTAB (dodecyltrimethyl ammonium bromide) and of the dimeric surfactant 12-2-12 (ethanediyl-1,2-bis(dodecyldimethyl ammonium bromide)) on raw silica (SiNa) and on HCl washed silica (SiH) has been investigated under “free” system conditions. The results have been shown that the amount of surfactant adsorbed at the point of zero charge and at saturation of the silica particles, the sodium ions released by the surface and the decrease in critical micelle concentration (CMC) of the supernatant with respect to pure water are all larger for the raw silica than for the treated silica.

### 2.3.2 Molecular Structure of the Surfactant being Adsorbed

Structure of the surfactant being adsorbed onto solid surface is another critical factor affecting adsorption and adsolubilization. It is important whether it is ionic or nonionic, and whether the hydrophobic group is long or short, straight-chain or branched, aliphatic or aromatic.

Esumi *et al.* (1996) studied the adsorption of quaternary ammonium cationic surfactants with one, two, and three alkyl chains on silica by measuring adsorption density, and dispersion stability. The adsorbed amount at saturation decreased with increasing chain number of the surfactant. Under a constant feed concentration of 2-naphthol, the adsolubilized amount of 2-naphthol increased, reached a maximum, and then decreased with single-chain or double chain surfactant concentration. The ratio of amount of 2-naphthol adsolubilized to the adsorbed amount of surfactant on silica for the double-chain and triple-chain surfactants were not so different and were quite large compared to that for the single-chain surfactant. In addition, from the two-step adsorption-adsolubilization procedure, it was found that the double-chain or triple-chain surfactant adsorbs strongly on the silica surface.

Subsequently, Esumi *et al.* (1997) studied adsorption and adsolubilization of cationic surfactant with different structures on clay (laponite). As an adsolubilize, 2-naphthol one of the representative toxic substances was employed. The results showed that adsorption of cationic surfactant increased from 3RdienQ to 1RQ in the layer of laponite, resulting in the layer broadening, where the adsorption by 2RenQ and 3RdienQ made the layer much larger than that by 1RQ. Most of 2-naphthol molecules as the feed concentrations were adsolubilized in the surfactant-adsorbed layer.

### 2.3.3 Environment of the Aqueous Phase

Properties of the aqueous phase such as pH that usually causes marked changes in the adsorption of ionic surfactants onto charged solid substrate. As the pH of the aqueous phase is lowered, a solid surface will usually become more positive, or less negative, because of adsorption onto charged sites of protons from the solution, with consequent increase in the adsorption of cationic. The reverse is

true when the pH of the aqueous phase is raised. These effects are shown markedly for mineral oxide, such as silica and alumina, and by wool and other polyamide. Change in the pH also may affect surfactant molecules, notably those containing carboxylate group (soap) or nonquaternary ammonium group. In these cases, change in the pH may convert the surfactant from one containing an ionic group capable of strong adsorption onto oppositely charged sites on the adsorbent to a neutral molecule capable of adsorption only through hydrogen bonding or dispersion forces. Change in pH also may affect nonionic surfactants, notably those having polyoxyethylene chain, because the ether linkage in these chains can be protonated at low pHs, yielding positively charged grouping that may adsorb onto negatively charged substrate. Moreover, the effect of the ionic strength on the adsorption is also very important to study because it can change the CMC, the effect being more pronounced for anionic and cationic than for zwitterionic surfactant and more pronounced for zwitterionics than for nonionic.

Monticone and Treiner (1995) studied effect of pH and ionic strength on the adsorption of cetylpyridinium chloride and the coadsorption of phenoxypropanol at a silica/water interface. The effects of pH and ionic strength on both of these phenomena were investigated. It was shown that the solute partition coefficient between the adsorbed aggregates and the solution was independent of pH and of ionic strength and was equal to the partition coefficient of the classical micellar solubilization effect for the same solute/surfactant system.

Subsequently, Behrends and Herrmann (1998) studied effect of pH and ionic strength on the adsorption of hexadecyltrimethyl ammonium bromide on silica. They also investigated the partition of anthracene between aqueous solution and silica-gel surface. Three different experimental conditions regarding pH and ionic strength (I) were investigated: pH=5 at  $I=10^{-3}$  mol/L and  $I=10^{-1}$  mol/L and pH=8 at  $I=10^{-3}$  mol/L. The results showed that the highest partitioning was observed for pH=5 and  $I=10^{-3}$  mol/L ( $1.3 \times 10^{-8}$  mol/m<sup>2</sup>) and decreased at elevated pH or salt concentration.

Monticone *et al.* (2000) investigated effect of pH on the coadsorption of weak acids to silica/water and weak base to alumina/water interfaces as induced by ionic surfactants. The effect of pH changes on the coadsorption effect for both

types of systems was studied in a pH range between 3 and 9. The surfactant concentration was kept constant corresponding to the isotherm region of a low surface coverage. Solute partition coefficient ( $P_{ads}$ ) and binding constant ( $K_B$ ) were also determined. It was shown that in all cases the solute coadsorption reached a maximum level at a pH value equal to the pK of the acids or of the bases. It was argued that the initial pH changes induced the dissociation of the solutes and a favorable interaction with the adsorbed surfactant ions. However as the pH further changed and the silica and alumina surfaces became increasingly ionized, these ionic sites were expected to be responsible for a repulsion effect on the dissociated solute species, hence the coadsorption reached its maximum. A simple thermodynamic model, which depending only upon chemical equilibria and the corresponding constants  $P_{ads}$ ,  $K_B$ , and pK was shown to fit well the experimental data providing that  $K_B$  was assumed to be a function of the solution proton activity.

Behrends and Herrmann (2000) studied the adsolubilization of anthracene on surfactant covered silica in dependence on pH: indications for different adsolubilization in admicelle and hemimicelle. They studied the distribution of anthracene between aqueous solution and silica gel covered with the cationic surfactant hexadecyltrimethylammonium bromide (HDTMA) in batch experiments as a function of the adsorption density of HDTMA and in dependence on pH. It was observed that the partitioning constant ( $K$ ), normalized on the content of organic carbon in the surfactant coverage was not only a function of the surface concentration but also depended on pH. At low concentrations of adsorbed HDTMA, no adsolubilization of anthracene was measured.

Pradubmook (2001) studied the effect of pH on adsolubilization of a cationic surfactant, cetyltrimethyl ammonium bromide (CTAB), on precipitated silica and adsolubilization of toluene and acetophenone in CTAB at two pH values. Both single-solute and mixed-solute systems were investigated using batch liquid adsorption at pH 5 and pH 8. The results from the adsorption of CTAB revealed that increasing pH led to high amounts of surfactant adsorbed on the precipitated silica. In the single solute system, the adsolubilization of both solutes increased with increasing equilibrium concentration of the solute in the aqueous phase. For toluene, pH appeared to have little effect on the adsolubilization. In contrast, the pH effect

was more pronounced in the case of acetophenone as indicated by significant increase in the acetophenone adsolubilization when pH was increased from 5 to 8. In the mixed solute system, the presence of acetophenone had insignificant effect on toluene adsolubilization whereas the presence of toluene had synergistic effect on acetophenone adsolubilization. Moreover, the analyses through the use of the adsolubilization equilibrium constant ( $K$ ) suggested that toluene adsolubilized into both the palisade layer and core of admicelle while acetophenone adsolubilized into palisade layer only.